

Quick and Green Procedure for the Quantification of Chromium in an Anionic Surfactant System

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Abstract

This study aims to establish a facile, user-friendly, accurate, and repeatable spectrophotometric detection method for Cr(III) ions in trace quantities. The method utilises reagent 1-nitroso-2-naphthol (NNPh) in a sodium dodecyl sulphate (SDS) 1.0 % micellar solution, replacing the old, time-consuming, and expensive solvent extraction method that employs hazardous solvents such as carbon tetrachloride and chloroform. SDS surfactant is used to solubilise indissoluble chelates, making the proposed technique easy, rapid, and environmentally friendly. The established method exhibits an improved linear calibration range, sensitivity, limit of detection, and selectivity compared to earlier spectrophotometric methods employing different complexing agents. The stoichiometric ratio between Cr and NNPh was observed to be 1 : 3. The molar absorption coefficient (ϵ) was determined to be $2.05 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 579 nm. The limits of detection for Cr(III) was measured as 3.49 ng l^{-1} . A calibration linear curve was achieved in the concentration range of $0.5\text{--}5.0 \mu\text{g ml}^{-1}$. Results obtained showed good comparison with the results obtained by atomic absorption spectrometry. The developed method has been adapted for the analysis of Cr(III) in various alloys, pharmaceutical, environmental, and biological samples.

Keywords

Chromium, micellar solution, 1-nitroso-2-naphthol, spectrophotometry, sodium dodecyl sulphate

1 Introduction

Metals play an important role in environmental and biological systems,¹ many metal ions, such as Zn(II), V(III), Cr(III) and Mn(II) are essential for human and other living organisms. Conversely, metals like arsenic, cadmium, lead, and mercury are toxic to living beings at certain concentration levels.^{2,3} Even essential metal ions can become toxic at elevated concentrations.⁴ Chromium, for instance, is essential for humans and other natural systems,⁵ being a steel grey, shiny, rigid, and fragile transition metal.⁶ Its name is derived from the Greek word χρῶμα, chrōma, meaning colour, due to the extensive colouring of many chromium compounds. Chromium is a vital mineral that the body cannot produce on its own, but must be acquired through dietary sources. Chromium is a mineral found in two forms,⁷ but only Cr(I-II) is utilised by the body and is present in food sources.⁸ It is essential for carbohydrate and fat breakdown,⁹ supporting brain function and other bodily processes.¹⁰ Cr also supports the action of insulin and the breakdown of glucose.¹¹ It is a metal element, which humans require in very small amounts. Brewer's yeast, broccoli, and liver are good sources.¹² Supplementation with chromium can increase muscular mass, weight loss, and glucose control.¹³ Its deficiency may potentially be associated with certain health disorders.¹⁴

Metallic chromium is highly valued due to its resistance to corrosion and rigidity.¹⁵ The addition of chromium metal

to steels revolutionised steelmaking, producing stainless steel highly resistant to corrosion and discolouration.¹⁶ Cr is not stable in O_2 . It immediately forms a fine layer of oxide that is impervious to O_2 and shields the metal.¹⁷ Chromium's chief applications include metal ceramics, alloys, and chrome coating.¹⁸ Chromium is used in metallurgy to provide resistance against corrosion and a lustrous finish;¹⁹ in paints and dyes,²⁰ in the production of artificial rubies;²¹ it serves as a catalyst for leather dyeing and tanning;²² it is used in the production of brick firing moulds;²³ as well as in the manufacture of magnetic tape.²⁴ Cr is extracted from the ore chromite (FeCr_2O_4).²⁵

Various methods exist for the determination of Cr(III) ions, such as UV/Vis spectrophotometry,²⁶ flame atomic absorption spectroscopy,²⁷ atomic absorption spectroscopy,²⁸ inductively coupled plasma atomic emission spectrometry²⁹ etc. Many of these methods are costly due to the high price of tools, time-consuming, and tedious. New methods are required for the trace-level determination of chromium ions, with the spectrophotometric technique being prevalent due to its simplicity, precision, speed, and inexpensive instruments. In UV-Vis spectrophotometry, metal ions are determined using chelating agents, where the metal reacts with a derivatising agent to form an insoluble metal complex that is solubilised through solvent extraction. Numerous spectrophotometric approaches for analysis of metals are available to replace the previous method of solvent extraction with the use of a micellar system.³⁰ Micellar methods have shown enhancement in the analytical characteristics of metal analysis by solubilising the complex.³¹ Recently, some spectrophotometrical procedures of lower

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sensitivity and selectivity have been developed for estimation of Cr(III) ions. In this study, we present a sensitive, rapid, selective, and appropriate procedure for trace analysis of Cr(III) using 1-nitroso-2-naphthol (NNPh) in 1.0 % sodium dodecyl sulphate (SDS) surfactant. This procedure was successfully employed for the determination of Cr(III) ions in various biological and environmental samples.

2 Experimental

UV-Vis Cecil CE 9500 spectrophotometer having quartz cells with path length of 10 mm, FT-IR spectrophotometer, atomic absorption spectrophotometer, and pH/conductivity meter (model Sension156 HACH Company, USA) were used in this research.

2.1 Preparation of reagents

The Cr(III) ion stock solution ($1000 \mu\text{g l}^{-1}$) was prepared in double-distilled water using high-purity salts supplied by Merck. Other solutions of metal ions were also prepared from their chloride and nitrate salts to study the effect of interfering analytes. The NNPh solution was prepared by adding 75 mg into a 50-ml flask, dissolving it in the least amount of ethyl alcohol, and adjusting the volume with 1.0 % SDS up to the mark.³² The 1.0 % SDS solution was prepared by taking 1.00 g of SDS in a 100-ml graduated flask and making up the volume with H_2O . Buffers with pH values ranging from 1 to 10 were prepared following the methods defined by Perrin,³³ involving the addition of appropriate amounts of hydrochloric acid (HCl) and potassium chloride (KCl) for pH 1.0 to 4.0, acetic acid (CH_3COOH) and sodium acetate (CH_3COONa) for pH 5.0 to 6.0, potassium dihydrogen phosphate (KH_2PO_4) and sodium hydroxide (NaOH) for pH 6.5 to 8.0, and hydrochloric acid (HCl) and sodium borate for pH 9.0 to 10.0.

2.2 General method for Cr(III) ions determination

Solutions containing concentrations of Cr(III) ions ranging from 0.06 to $10 \mu\text{g ml}^{-1}$, NNPh solution at 185 ppm ($185 \mu\text{g ml}^{-1}$), 2 ml of buffer solution (pH 8), and 2 ml of 1.0 % SDS solution were mixed in a 10-ml calibrated flask. The solutions were shaken well and double-distilled water was added up to the mark. The absorbance of Cr(III)-NNPh complex was recorded at λ_{max} 579 nm against NNPh as the blank.

2.3 Cr(III) ions investigation from water

A tap water sample from Ghotki city was collected, filtered using $0.45 \mu\text{m}$ filter paper, and acidified by adding 2 ml of concentrated HNO_3 to avoid precipitation. Chromium metal was added in the measuring flask, along with 2 ml of 185 ppm NNPh, 2 ml of pH 8 buffer solution, and 2 ml of SDS 1.0 %. The absorbance of the complex was then measured. The results are presented in Table 4.

2.4 Chromium determination from alloy

In a 25-ml beaker, 2 g of chromel reference substance was set, followed by the addition of 15 ml of concentrated HCl and 5 ml of concentrated HNO_3 . The sample solution's volume was reduced to 5 ml on a hot plate. Then, 10 ml of concentrated HCl was added, the sample was filtered, and the obtained filtrate was diluted to 25 ml with distilled water. The sample was transferred to a measuring flask. Subsequently, 2 ml of 185 ppm NNPh, 2 ml of pH 8 buffer solution, and 2 ml of 1.0 % SDS were added into the flask for complex formation. The absorbance was measured with a spectrophotometer. The results are presented in Table 5.

2.5 Chromium analysis from a reference sample

For each certified reference material (GBW 07605 Tea and GBW 0703 bush branches), 10 g was digested in 10 ml HNO_3 with 2 ml H_2O_2 in a microwave oven, diluted with deionised water, and filtered. The samples were transferred to a flagon, mixed with 2 ml of 185 ppm NNPh, and 2 ml of SDS was added. The complex absorbance was measured with a spectrophotometer, and the results are presented in Table 6.

2.6 Chromium analysis from a real sample

Two grams each of fish, white cheese, beef, black tea, and wheat were digested in a microwave oven with 10 ml of HNO_3 and 2 ml of H_2O_2 . The obtained solution was diluted to 50 ml with deionised water and filtered. The samples were transferred to a flask, mixed with 2 ml of 185 ppm NNPh, followed by the addition of 2 ml of appropriate buffer and 2 ml of SDS. The complex's absorbance was measured with a spectrophotometer, and the results are given in Table 6.

2.7 Chromium determination in pharmaceutical samples

A 25-g multivitamin tablet was ground finely and digested with 10 ml of concentrated nitric acid and 2 ml of H_2O_2 . The mixture was evaporated to dryness, and the residue was leached with 0.5 M H_2SO_4 and deionised water was added. The sample was then transferred to a measuring flask, and 2 ml volumes of 185 ppm NNPh, 2 ml of pH 8 buffer solution, and 2 ml of 1.0 % SDS were added for complex formation. The complex absorbance was measured with a spectrophotometer. The results were compared and are given in Table 3.

2.8 Chromium investigation in standard alloys

Five millilitres each of NIST 1643 and NIST 1643 were digested in 10 ml of concentrated HNO_3 , 10 ml of 20 % H_2SO_4 , and 2 ml of H_2O_2 . The solutions were evaporated and reduced; the sample was diluted, neutralised and filtered. The sample was then transferred to a flask; 2 ml of 185 ppm NNPh, 2 ml of buffer, 2 ml of 1 % SDS,

and tartrate masking agents were added. The complex's absorbance was measured, and the data are given in Table 7.

3. Results and discussion

3.1 Spectrophotometric analysis of chromium with NNPh reagent

Chromium(III) ions give coloured complexes in reaction with NNPh. NNPh exhibited n to π^* transition, and due to this transformation of electronic charge, NNPh displayed a sharp absorption peak. The oxygen atom of the $-OH$ and nitrogen of the $-N=O$ group in NNPh donate electron pairs to the chromium ion. The structure of the bonding sites of NNPh with the metal ion is shown in Fig. 1.

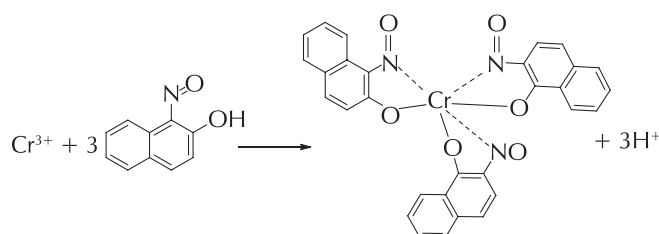


Fig. 1 – Proposed reaction of Cr(III) with NNPh forming $Cr[NNPh]_3$ complex

3.2 UV-Vis electronic spectra

1-Nitroso-2-naphthol exhibited a sharp absorption peak with an absorption maximum at λ_{max} 377.0 nm in a 1.0 % SDS micellar solution in the UV-Vis region of the spectrum as a result of the n to π^* electron transition. The charge transformation occurred from ligand to ligand ($L \rightarrow LCT$), as illustrated in Fig. 2.

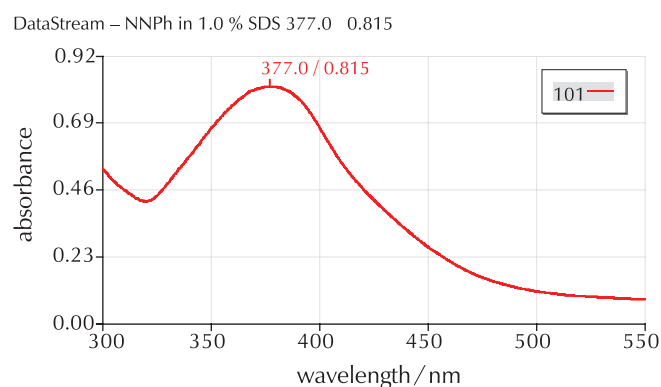


Fig. 2 – UV-Vis spectrum of NNPh in 1.0 % surfactant

The UV-Vis spectrum of Cr(III)-NNPh complex indicates a bathochromic shift in the bands of NNPh, shifted by 202 nm to a longer wavelength due to the n to π^* electron

transition. Ligand to metal charge transfer ($L \rightarrow MCT$) occurred from the filled orbital of chelate to the vacant $d\pi$ orbital of chromium at λ_{max} 579 nm. These observations indicate that the nitrogen atom of the $O=N-$ and the oxygen atom of the $-OH$ group of NNPh, upon deprotonation, participated in bonding for NNPh-complex formation, as illustrated in Fig. 3.

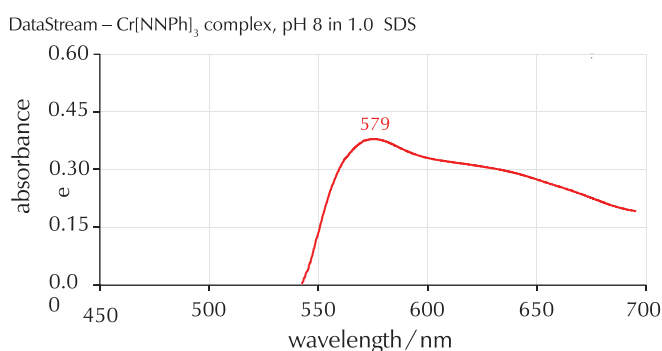


Fig. 3 – UV-Vis spectrum of $Cr[NNPh]_3$ complex

3.3 Metal chelate composition

The metal ligand mole ratio was analysed using Job's method. Stoichiometric and molar ratios were obtained through the technique of continuous variation of metal and ligand ratios.³⁴ Metal complexes of Cr(III) were formed, and absorbance plots against the mole fraction of metal ions are shown Fig. 4. The obtained results indicated a mole ratio of 1 : 3 for Cr(III)-chelate. NNPh demonstrated the capability to form stable chelate complexes with Cr(III).

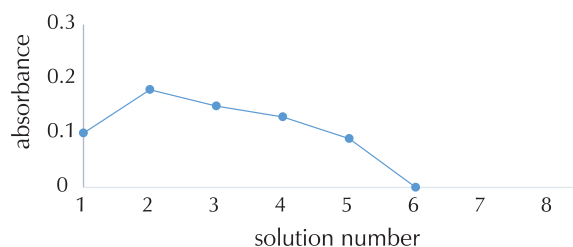


Fig. 4 – Mole ratio of Cr(III)-NNPh complex

3.4 Effect of 1-nitroso-2-naphthol concentration

The investigation focused on assessing the impact of NNPh concentration on complex-metal absorbance. This was achieved by varying the concentration of the reagent NNPh within the range of 5–80 mM, while maintaining a fixed concentration of metal ions at 1.0 mM. Notably, concentrations of NNPh ranging from 20–50 mM exhibited consistent maximum absorbance, indicating optimal conditions for complex formation. The optimised NNPh concentration, as depicted in Fig. 5, was consequently utilised throughout the entirety of the research endeavour.

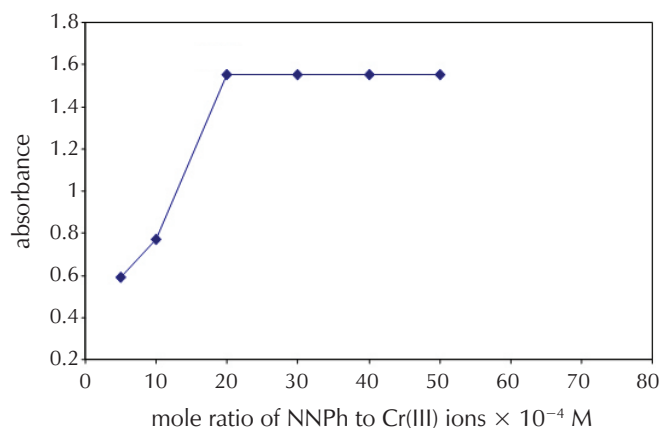


Fig. 5 – NNPh concentration effect on the absorbance of Cr(III) ions

3.5 Effect of surfactant

For surfactant optimisation, $2 \mu\text{g ml}^{-1}$ of Cr(III) metal ion solution, 2 ml of buffer, 2 ml of NNPh reagent, and 2 ml of 1.0 % SDS surfactant were mixed in a 10-ml volumetric flask, and absorbance was measured. It was observed that 2 ml of 1.0 % SDS showed constant maximum absorbance for Cr[NNPh]₃ chelate formation when the concentration of metal ions was kept at $2 \mu\text{g ml}^{-1}$. The 1.0 % SDS was optimised, exceeding the critical micelle concentration value of $8.3 \cdot 10^{-3}$ M, and this concentration was kept constant throughout the entire procedure.

3.6 Effect of pH value

To investigate the influence of pH on metal-chelate formation, pH values ranging from 1 to 14 were introduced into the solution during the formation of the metal-NNPh complex. Throughout this process, the metal concentration and NNPh remained constant across a series of volumetric flasks. The pH at which constant absorbance was observed indicated the optimised λ_{max} for the study of metal-chelate formation. The variation in pH altered the spectra of the metal-NNPh complex. The sensitivity and spectra of the metal-NNPh complex absorbance were found to either decrease or increase with changes in pH. Notably, pH 8 was identified as the optimum pH for Cr(III) based on the constant absorbance observed throughout the entire study, as illustrated in Fig. 6.

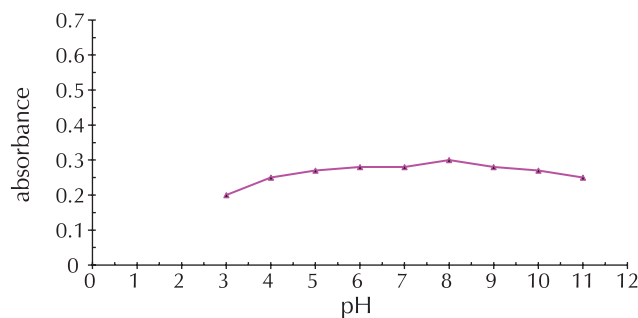


Fig. 6 – pH effect on absorbance of Cr(III)-NNPh complex

3.7 Effect of time

The stability of metal-complex was studied and demonstrated rapid constant absorbance at room temperature, with the absorbance of the metal-chelate remaining unaltered for 24 h.

3.8 Calibration curve

The calibration line of Cr(III) exhibited linearity in the concentration range of $0.5\text{--}5.0 \mu\text{g l}^{-1}$ with an R^2 value of 0.9993 at λ_{max} 579 nm (Fig. 7).

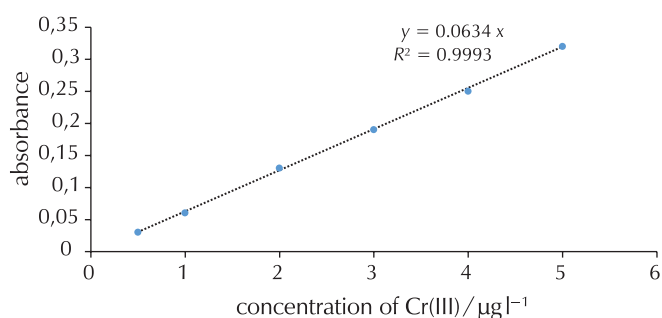


Fig. 7 – Calibration line of Cr(III)-NNPh

3.9 Molar absorption

The calibration line displayed an average coefficient of molar absorption as $2.05 \cdot 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ for Cr(III) at λ_{max} 579 nm, as provided in Table 1. The molar absorption for metal-chelate showed a better improvement compared to previously reported methods.^{26,36}

3.10 Sandell's sensitivity

The value for Sandell's sensitivity (S.S.) was determined to be 3.49 ng cm^{-2} for Cr(III), as presented in Table 1. The calculated data calculated represents a more significant improvement than stated earlier.

3.11 Limit of detection

The limit of detection (D.L.) was determined to be 3.49 for Cr(III), as presented in Table 1. The data value demonstrated better enhancement than reported.

3.12 Interference from foreign ions

In metal-chelate formation, the interference of various cations and anions was investigated. Potassium thiocyanate (KSCN), sodium tartrate, and potassium chlorate (KClO_3) interfered less, and showed beyond $800 \mu\text{g l}^{-1}$, confirming interference in complex absorbance for Cr(III), Mn(II), V(III), and Cd(II) at their minute level. Masking agents such as ascorbic acid, ethylenediaminetetraacetic acid (EDTA),

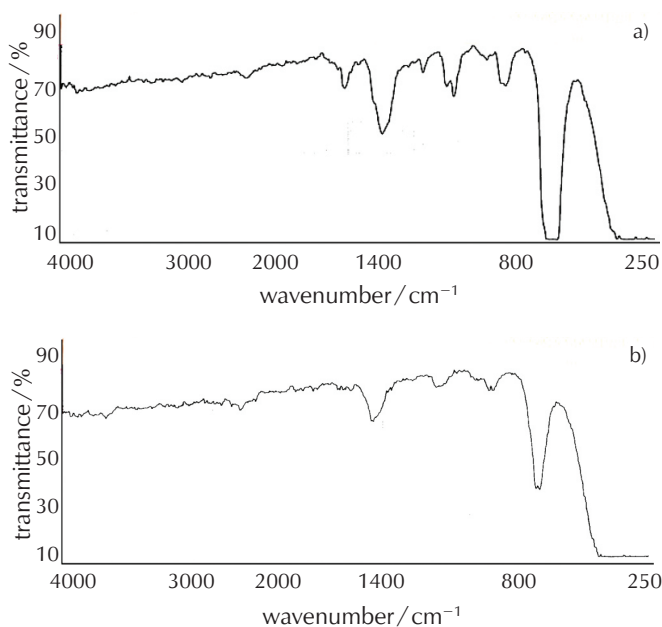
Table 1 – Analytical parameters of chromium-NNPh in 1.0 % SDS

Parameters	Chromium
Beer's law range $\mu\text{g l}^{-1}$	0.5–5.0
Absorption maximum	579 nm
Molar absorptivity	$2.05 \cdot 10^4 \text{ mol cm}^{-1}$
pH	8
1.0 % SDS	2.0 ml
NNPh concentration	$5.0 \cdot 10^{-4} \text{ mol l}^{-1}$
M : L ratio	1 : 3
S.S. ng cm^{-2}	3.49
D.L. ng l^{-1}	3.49
R^2	0.999

and dimethyl glyoxime were employed to reduce interference from foreign ions.³⁵ The diverse effect of analytes on Cr(III) complex formation was mitigated by the masking agent ammonia buffer, as shown in Table 2.

3.13 FTIR spectra

FTIR of NNPh revealed a stretching band at 2998 cm^{-1} for $\nu(\text{O}=\text{N})$ $\nu(\text{O}-\text{O})$. The band of $\nu(\text{C}-\text{N})$, $\nu(\text{N}=\text{O})$, and $\delta(\text{C}-\text{OH})$ were measured at 1718, 1545, 1221, 1099, and 898 cm^{-1} wave number. Absorption bands in the bending

**Fig. 8** – (a) FTIR spectra of NNPh derivatising agent in CHCl_3 and (b) FTIR spectra of Cr(III)-NNPh in CHCl_3 **Table 2** – Interference of foreign ions/salts in absorbance of Cr(III)-NNPh complex

Ions/salts	Chromium/ $\mu\text{g l}^{-1}$
Sodium tartrate, KSCN, KClO_3	800
Zn(II)	50
Al(III)	10
Mn(III)	5
Sodium citrate	500
Pb(II)	3
$\text{Na}_2\text{C}_2\text{O}_4$	200
Cd(II)	5
Cr(VI)	8
KCN	50
Mg(II)	600
V(III)	5
Mn(II)	200
Cr(III)	–
Cd(II)	2

region at 1095 , 900 , and 800 cm^{-1} of nitroso and naphthyl are shown in Fig. 8(a). The band of metal-chelate bonding is changed from NNPh reagent. The $\nu(\text{N}=\text{O})$ stretching band showed an increase of $20\text{--}30 \text{ cm}^{-1}$ due to bonding with N of the nitroso group. The $\nu(\text{C}-\text{O}-\text{H}\dots\text{N}=\text{O})$ stretching band increased to a high band by $20\text{--}30 \text{ cm}^{-1}$ next to 1750 , and 1250 cm^{-1} $\nu(\text{O}=\text{N})$ bond between metal and NNPh through $\nu(\text{M}-\text{O})$. The change in absorption bands showed bonding between metal and NNPh through chelation via the $\text{M}-\text{O}-\text{H}$ and $\text{M}-\text{N}$ sites. The newest peaks were observed at 1440 cm^{-1} for the $\nu(\text{M}-\text{O})$ in the Cr(III)-chelate, as presented in Fig. 8(b).

3.14 Validation of the method

The developed technique was validated through standard addition test % recovery, comparison with AAS, and with reference materials at a confidence interval of 95 %. The results obtained demonstrated good agreement with all aforementioned official methods, indicating good reproducibility, accuracy, and precision, as shown in Tables 3–6. The developed method exhibited greater sensitivity and selectivity than previously reported spectrophotometric techniques for metal ion determination. The method presented advantages over the earlier extraction procedure, being selective, straightforward, sensitive, rapid, and versatile. A simple, rapid, and inexpensive technique was developed for the investigation of chromium at minute levels using NNPh in a micellar 1.0 % SDS solution. The proposed procedure was applied for the investigation of Cr(III) ions in biological, pharmaceutical, environmental, industrial, certified material, and water samples.

Table 3 – Investigation of Cr(III) in reference materials

Sample	Metal ion	Developed method/ $\mu\text{g l}^{-1}$	%RSD	AAS method/ $\mu\text{g l}^{-1}$	%RSD	Recovery
Cr(III)-GFT* tablet (27.0 mg/tablet)	Cr(III)	26.98	0.5	26.97	0.5	99.89

* Glucose Tolerance Factor (GFT)

Table 4 – % recovery (R) of a known quantity of metals mixed in water samples

Analyte ion	Added content/ $\mu\text{g l}^{-1}$	Found/ $\mu\text{g l}^{-1}$	% Recovery
Cr(III)	3.62	3.61	99

Table 5 – Investigation of Cr(III) in alloy samples

Alloy	Composition of Cr(III)/ $\mu\text{g g}^{-1}$	Found/ $\mu\text{g g}^{-1}$
Chromel A Ni-Cr 80-20	2.0	1.9 ± 0.1

Table 6 – Analysis of chromium in certified materials and food samples

Samples	Certified value/ $\mu\text{g g}^{-1}$	Found value/ $\mu\text{g g}^{-1}$
GBW 0703 bush branches and leaves	2.6	2.7
GBW 0760 tea	0.8	0.81
Chromium in food samples		
Black tea	–	0.24
Boiled wheat	–	1.50
Fish	–	1.95
White cheese	–	0.79
Cows meat	–	0.67

Table 7 – Analysis of Cr in standard reference materials

Sample	Certified/ $\mu\text{g l}^{-1}$	Found/ $\mu\text{g l}^{-1}$	
		Cr(III)	Cr(VI)
NIST-1643	18.6	18.4	–
NIST-1643	19.0	18.9	–

Table 8 – Comparison of methods for the determination of chromium using NNPh

Metal ion	Procedure	Refs
Cr(III)	linear range 0.2 to 2.4 $\mu\text{g l}^{-1}$, λ_{max} 575 nm, ϵ $1.46 \cdot 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$	36
Cr(III)	λ_{max} 295 nm, ϵ $5.4 \cdot 10^3$ in Triton X-100	26
Cr(III)	D.L. 3.49 $\mu\text{g l}^{-1}$, ϵ $2.05 \cdot 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$, λ_{max} 579 nm in 1.0 % SDS	Method developed in this study

4 Conclusion

This developed procedure for the quantification of Cr(III) ions at the trace level is quick, green, novel, non-extractive, sensitive, and versatile. It is environmentally friendly, demonstrates higher selectivity and sensitivity, and replaces previous solvent extraction methods that are slow, expensive, and hazardous. The results show significant improvement in sensitivity and molar absorption compared to reported methods, as shown in Table 8. The proposed method was successfully employed to determine Cr(III) ions in biological, environmental, real, and industrial samples.

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SAŽETAK

Brz i ekološki postupak za kvantifikaciju kroma u anionskom površinski aktivnom sustavu

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Cilj ovog rada je razviti jednostavnu, točnu i ponovljivu spektrofotometrijsku metodu analize Cr(III) iona u tragovima. Metoda primjenjuje reagens 1-nitrozo-2-naftol (NNPh) u 1,0 % micelarnoj otopini natrijeva dodecil sulfata (SDS), zamjenjujući staru, dugotrajnu i skupu metodu ekstrakcije otapalom koja upotrebljava opasna otapala kao što su ugljikov tetraklorid i kloroform. SDS se upotrebljava u solubilizaciji prethodno netopljivih kelata, čineći predloženu metodu jednostavnom, brzom i ekološki prihvatljivom. Razvijena metoda ima šire linearno područje te bolju osjetljivost, granicu detekcije i selektivnost u usporedbi s dosadašnjim spektrofotometrijskim metodama koje su upotrebljavale različite kompleksirajuće agense. Stehiometrijski omjer između metala kroma i liganda NNPh je 1 : 3. Određen je molarni apsorpcijski koeficijent (ϵ) $2,05 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ pri λ_{max} 579 nm. Granica detekcije za Cr(III) iznosi $3,49 \text{ ng l}^{-1}$. Kalibracijski pravac dobiven je u rasponu koncentracija od 0,5 do $5,0 \text{ } \mu\text{g ml}^{-1}$. Dobiveni rezultati podudaraju se s rezultatima dobivenim atomskom apsorpcijskom spektrometrijom. Razvijena metoda prilagođena je za analizu Cr(III) u različitim legurama, farmaceutskim, okolišnim i biološkim uzorcima.

Ključne riječi

Krom, micelarna otopina, 1-nitrozo-2-naftol, spektrofotometrija, natrijev dodecil sulfat

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